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AUTHOR(S):

Shigematsu, Toshihiko; Takewa, Naoko; Ohtsuki, Masato; Watanabe, Kohji; Bando, Yoshichika; Nakanishi, Norihiko

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Hydrogenation of Carbon Monoxide by Fe-Ni Alloy Catalyst

Toshihiko SHIGEMATSU*, Naoko TAKEWA*, Masato OHTSUKI**,***, Kohji WATANABE**,****, Yoshichika BANDO** and Norihiko NAKANISHI*

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Differences in carbide phases formed in $Fe_{1-x}Ni_x$ alloy catalysts during the hydrogenation of carbon monoxide play important role on the product selectivity. The ratio of alkens to alkans in C_2–C_4 hydrocarbons became lower as the bcc $Fe_{1-x}Ni_x$ catalyst was converted into the ε' carbide, $(Fe_{1-x}Ni_x)_{2.2}C$. On the other hand, the ratio of alkens to alkans in C_2–C_4 hydrocarbons became higher with the increase of time after synthesis was started for the fcc $Fe_{1-x}Ni_x$ catalyst, where carbon atoms dissolved into a fcc lattice and formed a fcc solid solution, $Fe_{1-x}Ni_xC_y$.

KEY WORDS: Fischer-Tropsch synthesis/ Product selectivity/ Carbide formation/

INTRODUCTION

In Fischer-Tropsch synthesis, it has been reported that the catalytic properties such as the activity and product selectivity were changed sharply by the alloying of two metal catalysts. Many studies have been dealing with the Fe-Ni alloy catalysts, that are not stable during the hydrogenation of CO, but they change their states during synthesis.[1-2] There existed significant differences in the carbide phases formed during synthesis depending on the original crystal structures of $Fe_{1-x}Ni_x$ catalysts.[2] The bcc $Fe_{1-x}Ni_x$ catalyst was converted into the ε' carbide, $(Fe_{1-x}Ni_x)_{2.2}C$ during synthesis. On the other hand, no carbides were formed from the fcc $Fe_{1-x}Ni_x$ catalyst. Carbon atoms dissolved into the fcc lattice and formed the fcc solid solution, $Fe_{1-x}Ni_xC_y$. This difference in the carbide phases formed during synthesis will play important role on determining the catalytic properties of hydrogenation of CO. In this work we investigated the catalytic properties of $Fe_{1-x}Ni_x$ catalysts and found that there are distinct differences on the product selectivity between the bcc and fcc $Fe_{1-x}Ni_x$ catalysts in accordance with the differences in carbide phases formed during synthesis.

EXPERIMENTAL

Alloy catalysts used in this work were prepared from $Fe_{1-x}Ni_xC_2O_4 \cdot 2H_2O$.[2]

* 重松利彦，武輪直子，中西典彦：Department of Chemistry, Faculty of Science, Konan University, Higashinada-ku, Kobe 658.

** 大槻真人，渡辺宏二，坂東尚周：Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

*** Present Adress: Mitsubishi Metal Research Institute, Ohmiya, Saitama-ken 330.

**** Present Adress: R. & D. Laboratory-1, Nippon Steel Corporation, Kawasaki, Kanagawa-ken 211.

$Fe_{1-x}Ni_xC_2O_4 \cdot 2H_2O$ was precipitated from an aqueous solution of two sulfates containing Fe^{+2} and Ni^{+2} in a required composition with an oxalic acid at 343 K. Alloys of various compositions were prepared by the reduction of $Fe_{1-x}Ni_xC_2O_4 \cdot 2H_2O$ in hydrogen atmosphere prior to synthesis. The reactor consisted of a 6 mm i.d. Pyrex tube, typically containing 0.2 g of alloy catalyst, mounted in an electrically heated furnace. Reactions were carried out under differential conversion conditions with the maximum conversion of 5% at 101 kPa with an 1:1:3 mixture of CO, H_2 and N_2, respectively, at a total gas rate of 0.5 cm^3/s (STP). C_1–C_5 hydrocarbons in the effluent gas were analysed, using a gas chromatography (detector: FID, column: Gaskuropac 54). The catalysts before and after various periods of synthesis were characterized by X-ray diffraction (XRD), Mössbauer spectroscopy and scanning electron microscopy (SEM) measurements.

RESULTS AND DISCUSSIONS

The XRD and Mössbauer spectroscopy measurements of the alloy catalysts reduced at 573 K for 5.4 ks revealed that alloys with $x=0.08$ and 0.20 had bcc structure and alloys with $x=0.45$ and 0.85 had fcc structure. No oxide phases were observed in the XRD and Mössbauer spectra. The alloy with $x=0.20$ was a mixture of bcc and fcc phases after reduction at higher temperatures than 573 K. From these facts, catalytic reactions were carried out at 513 K, far below the reduction temperature. The mean particle sizes of the as-reduced catalysts estimated from the broadening of XRD lines by Scherrer's formula were about 50 nm, independent of composition. These values agreed well with those estimated from SEM and BET ($\sim$15 m^2/g) measurements. From these facts and rather narrow width of the Mossbauer lines ($\sim$0.5 mm/s), we can conclude that the $Fe_{1-x}Ni_x$ catalyst used in this work had small concentration flactuation between the alloy particles and also in an alloy particle.

Figure 1 shows the hydrocarbon product distribution after various periods of synthesis using the bcc $Fe_{0.80}Ni_{0.20}$ as a catalyst. A rate of the CO hydrogenation to C_1–C_5 hydrocarbons, expressed as a molar rate per gram of alloy for the $Fe_{0.80}Ni_{0.20}$ catalyst, is also shown in Fig. 1. The rate of CO hydrogenation showed a maximum value at 3.0 ks after the reaction was started and decreased gradually with the increase of time of catalyst utilization. In an early stage of synthesis (less than 3.0 ks of catalyst utilization), product selectivity slightly shifted toward a higher hydrocarbon content with the increase of time of catalyst utilization. From the Mossbauer spectroscopy and XRD measurements,[2] the catalyst was almost converted into the ε' carbide, $(Fe_{0.80}Ni_{0.20})_{2.2}C$, at 3.0 ks after the reaction was started. The reduced $Fe_{0.80}Ni_{0.20}$ catalyst is less active for the CO hydrogenation than the carburized catalyst and slightly favors methane formation (57% for the reduced catalyst and 53% for the carburized catalyst). After the bcc $Fe_{0.80}Ni_{0.20}$ catalyst was completely converted into the ε' carbide (more than 3.0 ks of catalyst utilization), the fraction of methane in C_1–C_5 hydrocarbons increased gradually with the increase of time of catalyst utilization. The deactivation of the CO hydrogenation

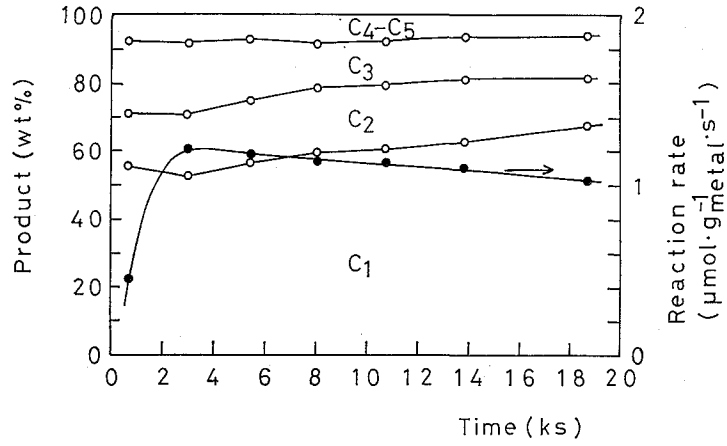

Fig. 1. Catalytic activity and selectivity in the CO hydrogenation over bcc $Fe_{0.80}Ni_{0.20}$ catalyst as a function of time of catalyst utilization. (513 K, 101 kPa, $H_2/CO=1.0$)

and the increase of methane fraction in C_1–C_5 hydrocarbons at this stage may be caused by the formation of carbon at the surface of the catalyst due to the dissociation of CO. These carbon atoms can be hydrogenated to methane and their rate of hydrogenation will be small relative to that of the CO hydrogenation.[3] The most notable difference in the product selectivity between the reduced and carburized catalyst is the ratio of alkens to alkans, as shown in Table 1. The selec-

Table 1 The ratio of alkens to alkans in the CO hydrogenation over the bcc $Fe_{0.80}Ni_{0.20}$ catalyst.*

Ratio of alkens to alkans	Time of catalyst utilization					
	0.6	3.0	5.5	8.2	10.8	13.8
C_2H_4/C_2H_6	4.2	14.0	15.6	15.6	18.5	19.0
C_3H_6/C_3H_8	0.8	1.5	1.7	2.0	2.3	2.3
C_4H_8/C_4H_{10}	2.1	3.0	3.0	3.0	3.0	3.0

* Reaction conditions: 101 kPa, $H_2/CO=1.0$, T=513 K.

tivity to the alkens product for the reduced $Fe_{0.80}Ni_{0.20}$ catalyst is higher than those for carburized catalyst. The decrease of alkens to alkans ratio in the carburized catalyst was the same as observed in the supported Fe catalyst.[4] After the catalyst was completely carburized, the ratio of alkens to alkans showed no change with the increase of time of catalyst utilization. The increase of surface carbon atoms showed no effect on the ratio of alkens to alkans. The bcc $Fe_{0.92}Ni_{0.09}$ catalyst showed same activation and deactivation behavior for the rate of CO hydrogenation, and the same product selectivity during synthesis.

Figure 2 shows the hydrocarbon product distribution using the fcc $Fe_{0.45}Ni_{0.55}$ as a catalyst. From the Mossbauer spectroscopy and XRD measurements on the fcc $Fe_{0.45}Ni_{0.55}$ catalyst, it was found that carbon atoms started to dissolve into the

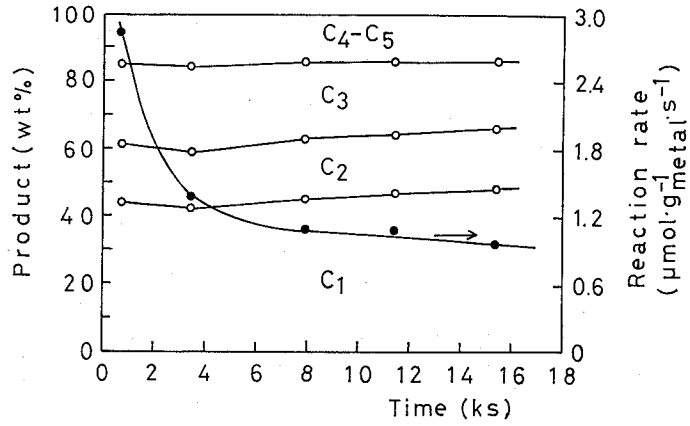

Fig. 2. Catalytic activity and selectivity in the CO hydrogenation over fcc $Fe_{0.45}Ni_{0.55}$ catalyst as a function of time of catalyst utilization. (513 K, 101 kPa, $H_2/CO=1.0$)

fcc lattice as soon as the catalyst was subjected to the hydrogenation of CO. Carbon atoms were homogeneously dissolved into the catalyst particles to the extent of their solubility limit (~5 at%),[2] at 7.2 ks after the reaction was started. The rate of CO hydrogenation decreased monotonously and the fraction of methane in C_1–C_5 hydrocarbons increased with the increase of time of catalyst utilization. This deactivation of the CO hydrogenation and the increase of methane fraction in C_1–C_5 hydrocarbons are also caused by the formation of surface carbon on the catalyst by the dissociation of CO. The alkens to alkans ratio was increased with the increase of time of catalyst utilization, as shown in Table 2. The fcc $Fe_{0.15}Ni_{0.85}$

Table 2 The ratio of alkens to alkans in the CO hydrogenation over the fcc $Fe_{0.45}Ni_{0.55}$ catalyst.*

Ratio of alkens to alkans	Time of catalyst utilization				
	0.6	3.6	7.8	11.7	15.3
C_2H_4/C_2H_6	14.0	2.6	1.9	1.6	1.5
C_3H_6/C_3H_8	1.3	0.3	0.2	0.2	0.2
C_4H_8/C_4H_{10}	2.7	2.0	1.5	1.1	0.9

* Reaction conditions: 101 kPa, $H_2/CO=1.0$, T=513 K.

catalyst produced mainly methane and small amount of C_2–C_5 hydrocarbons as shown in Fig. 3.

The notable differences in the catalytic properties between the bcc and fcc $Fe_{1-x}Ni_x$ catalysts are as follows.

1) In the bcc $Fe_{1-x}Ni_x$ catalysts, nickel content showed no effect on the product selectivity, but the fraction of higher hydrocarbons decreased with the increase of x in the fcc $Fe_{1-x}Ni_x$ catalyst. Ni is known as an excellent hydrogenation catalyst and produces mainly methane.[5] The increase of nickel content in the fcc $Fe_{1-x}Ni_x$ catalyst will increase the availability of hydrogen for the reaction. The bcc $Fe_{1-x}Ni_x$

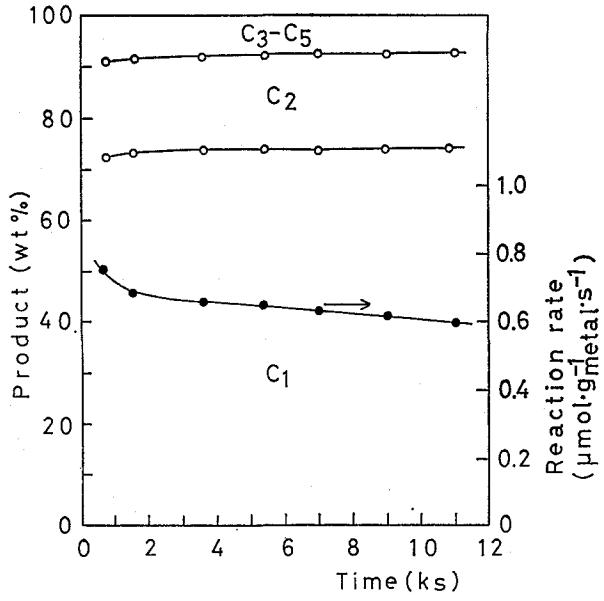

Fig. 3. Catalytic activity and selectivity in the CO hydrogenation over fcc $Fe_{0.15}Ni_{0.85}$ catalyst as a function of time of catalyst utilization. (513 K, 101 kPa, $H_2/CO=1.0$)

catalysts, which have smaller amount of nickel content, showed higher selectivity to methane than fcc $Fe_{0.45}Ni_{0.55}$ catalyst (57% for bcc $Fe_{0.80}Ni_{0.20}$ vs 44% for fcc $Fe_{0.45}Ni_{0.55}$). The difference in the electronic states between the bcc and fcc $Fe_{1-x}Ni_x$ alloy may affected on the product selectivity. The lowest selectivity to methane and the highest selectivity to C_2–C_5 hydrocarbon were achieved on the fcc $Fe_{0.45}Ni_{0.55}$ catalyst.

2) The alkens to alkans ratio decreased with the increase of time of catalyst utilization in the bcc $Fe_{1-x}Ni_x$ catalyst, and increased in the fcc $Fe_{0.45}Ni_{0.55}$ catalyst. Differences in the carbide phases formed in $Fe_{1-x}Ni_x$ catalysts during synthesis play important role on the ratio of alkens to alkans. The changes of the arrangement of metal atoms in the catalysts and the changes in the electronic states may be the origin of the change of alkens to alkans ratio with the increase of time of catalyst utilization.

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